

Dielectric Investigation on Newly Synthesized H – Shaped Liquid Crystalline Dimer

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Abstract

The present study reports the dielectric behavior of unusual H-Shaped liquid crystal dimer named *Bis[5-(4'-*n*-dodecyloxybenzoyloxy)-2-(4"-chlorophenylazo)phenyl]butylethers* (12-Cl-H4). The observations suggest that relaxation mode observed in MHz region follows the Cole-Cole theory for the given sample. Various dielectric parameters such as relaxation frequency, relaxation strength, dielectric permittivity, activation energy have been evaluated. The dielectric behavior of the given sample has been studied with variation in both temperature and frequency. Also a strong theoretical background has been depicted to minimize one of the liquid crystal defects (splay defect), with this new molecular topology. Thus, this new molecular topology could trigger a revolution in liquid crystalline devices and be used in future from application point of view.

Keywords

Liquid Crystal Dimer; Dielectric Permittivity; Relaxation Frequency; Activation Energy

Introduction

Liquid crystal posses many unique physical and optical properties, thus the importance of liquid crystals lies in their extensive use in display devices, as well as many other scientific applications [Brown, 1975 and Chong, 2007]. However, the use of liquid crystals in different devices depends on various dielectric as well as electro-optical parameters. A particular application of liquid crystals requires a particular set of parameters of liquid crystals in required range [Vill, 2006]. Researchers have made significant inroads into understanding the properties of liquid crystalline substances, but still the problem of predicting physical properties of liquid crystalline compounds based upon information on molecular shape and intermolecular

interaction remains one of the most fundamental issues in the liquid crystal physics [Yoshizawa et al., 2006 and Goodby et al.,1999]. The design of novel thermotropic liquid crystals involves suitable selection of a core fragment, linking group and terminal functionality. In 1907, Vorlander proposed a rule that the liquid crystalline state is obtained for the most linear of molecules]. Later, isometric rod like-or dislike-shape molecules used to be a fundamental prerequisite for conventional thermotropic liquid crystal formation because of steric packing considerations play an important role in this interesting state of soft matter [Mackenzie et al.,1998 and Kumar et al., 2009]. More recently, with the discovery of banana shaped liquid crystals, where bent molecules serve as core, interest in the incorporation of non linear units has gained importance from application point of view. A large number of bent core liquid crystal molecules have been synthesized and their analyses have been reported in the field of liquid crystal [Walba et al., 2000 and Newkome et al. ,1997].

Currently, molecular topology and microsegration have attracted much attention for producing unusual molecular structure such as supramolecular assemblies composed of super molecules i.e. oligomeric and dendritic liquid crystals [Rein et al., 1993 and Meier et al, 1975] Recently, dendritic liquid crystals have been investigated intensively, because functional dendrimers have rich super molecular chemistry and self assembling properties [Bottcher et al., 1978 and Blinov et al. , 1994]. The introduction of a bent shape in a molecular structure is another important strategy in the design of super molecules which exist in our liquid

crystalline sample discussed later. In addition, liquid crystal dimers have been the focus and targets of many researchers due to their remarkable and quite different phase transition properties to conventional liquid crystals; and being regarded as model compounds for main chain liquid crystals [Andersch et al., 1996 and Bailey et al., 2009]. A symmetrical or unsymmetrical dimer is formed when two chemically identical or non-identical anisometric segments, respectively, are connected covalently through a flexible spacer.

Lateral substitution at the centre of the mesogen increases the molar volume and decreases the liquid crystal packing density, thereby hindering their ability to form any kind of liquid crystalline phase if the mesogens is short, and smectic mesophases if the mesogen is more extended [Govind et al. 2001 and Varia et al., 2012].

There are several factors influencing the dielectric properties of liquid crystal materials, in which the value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors [Prajapati et al., 2007 and Dhar et al., 2002].

The present paper reports the dielectric properties of unusual H-Shaped liquid crystal dimer exhibiting two meso phases (SmC and SmX). The dielectric spectroscopy method is very well suited to study the rotational dynamics of molecules in liquid crystalline phases if the constituting molecules posses a dipole moment. The dielectric results show that sample follows Cole-Cole theory. The different dielectric parameters have been evaluated by Cole-Cole plots. The temperature dependence of different dielectric parameters such as dielectric permittivity; dielectric loss has also been reported. In addition to this activation, energy for the given sample has also been estimated. The dynamics of the dielectric relaxation process in molecules, in which internal rotation is possible, has been of interest to several research workers in the past.

Experimental Procedure

Material

The sample under investigation is H-shaped mesogenic dimer: Bis[5-(4'-n-dodecyloxybenzoyloxy)-2-(4"-chlorophenylazo)phenyl]butylethers (12-Cl-H4), that

has been prepared by the alkylation of 4-chloro-2'-hydroxy-4'-(4-n-alkoxybenzoyloxy) azobenzene with 1, 4-dibromo butane following the process reported in the literature. Energy-minimized balls and sticks model (MM2 models derived from CS Chem draw Ultra 7.0 software) of H-shaped liquid crystal (12-Cl-H4) is given in figure 1.

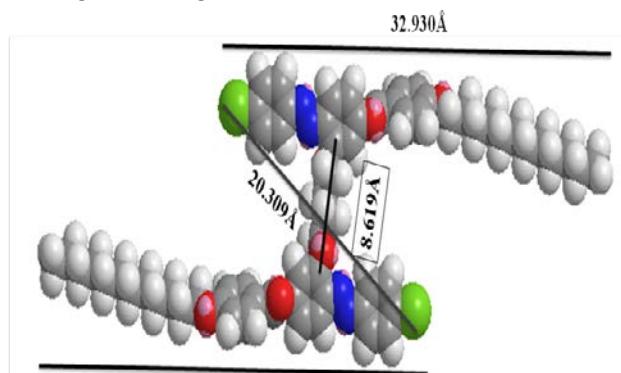
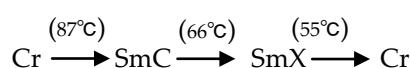


FIG. 1 ENERGY-MINIMIZED BALLS AND STICKS MODEL (MM2 MODELS DERIVED FROM CS CHEM DRAW ULTRA 7.0 SOFTWARE) OF H-SHAPED LIQUID CRYSTAL (12-CL-H4)

The phase transition scheme for the sample (12-Cl-H4) is given below:-



Preparation of Cell

Two similar cells having active area 49 mm², (sheet resistance and the visible light transmission are 10 Ω/mm² and more than 90%, respectively) were prepared by using transparent and highly conducting ITO-coated (Indium Tin Oxide), optically flat glass substrates used as electrodes. These electrodes provide a base to align the liquid crystal sample. To achieve a planar alignment, the electrodes were treated with a polymeric adhesion promoter (Nylon 6/6), and then rubbed unidirectionally with a velvet cloth. The thickness of the cell was maintained at 5 μm by means of Mylar spacers. The cells have been calibrated using standard AR grade liquids like benzene (C₆H₆) and carbon tetrachloride (CCl₄). The material was introduced into the cell by capillary action. Alignment of the sample was confirmed by placing the sample into crossed position of polarizing microscope CENSICO (7626). The correct and proper alignment of the liquid crystal molecules is extremely important for precise measurements of electrical properties and which, in turn, influences dielectric parameters. Thus, correct alignment plays an extremely important role in determining molecular geometry. The preparation of

sample cells with planar alignment has also been discussed in our earlier papers [Manohar et. al 2006, 2010, 2011].

Dielectric Permittivity Study

The dielectric behavior of the material has been studied by using a computer-controlled impedance/gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric parameters were measured as a function of frequency and temperature. In order to vary the temperature, a microprocessor-based heating device (Julabo-F25) has been used. The experiment was performed at very slow heating rate, and temperature was measured and controlled with accuracy of $\pm 0.01^\circ\text{C}$.

Result and Discussion

Different dielectric parameters of the sample have been determined using the Cole-Cole [Cole et al., 1941] dispersion equation given by

$$\epsilon^* = \epsilon'_{\infty} + \frac{\delta\epsilon'}{1 + (j\omega\tau)^{1-\alpha}} \quad (1)$$

Here $\delta\epsilon'$ is the dielectric strength of the material, ϵ'_{∞} is the high frequency limit of the dielectric permittivity, $\omega (=2\pi f)$ is the angular frequency, τ is the relaxation time and α is the distribution parameter. If the value of α is small and approaches zero, the above equation will satisfy the Debye type of relaxation phenomena, but for values more than 0.5, the above equation suggests the existence of more than one relaxation process.

The sample cell geometry introduces errors in the data in both the low and high ends of the frequency range investigated. Therefore, the experimental results required a low- and high-frequency correction. On separating real and imaginary parts of the equation (1) and adding high- and low- frequency correction parameters, we find

$$\epsilon' = \epsilon'_{dc} f^{-n} + \epsilon'_{\infty} + \frac{\delta\epsilon' [1 + (2\pi f\tau)^{1-\alpha} \sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} \quad (2)$$

and

$$\epsilon'' = \frac{\sigma_{dc}}{\epsilon_0 2\pi f^k} + \frac{\delta\epsilon' (f\tau)^{(1-\alpha)} \cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} + Af^m \quad (3)$$

Where σ_{dc} is the ionic conductance, ϵ_0 is the free space permittivity and f is the frequency, while n , m and k are the fitting parameters. The terms ϵ_{dc} , f^n and $\sigma_{dc}/\epsilon_0 2\pi f^k$ are added in equations (2) and (3) to correct for electrode polarization, capacitance, and ionic conductance at low frequencies. Term Af^m is added in equation (3) for high frequencies to correct for the ITO sheet resistance and lead inductance of the cell. By a least square fitting of the above equations using

experimental data, the low and high frequency errors have been removed.

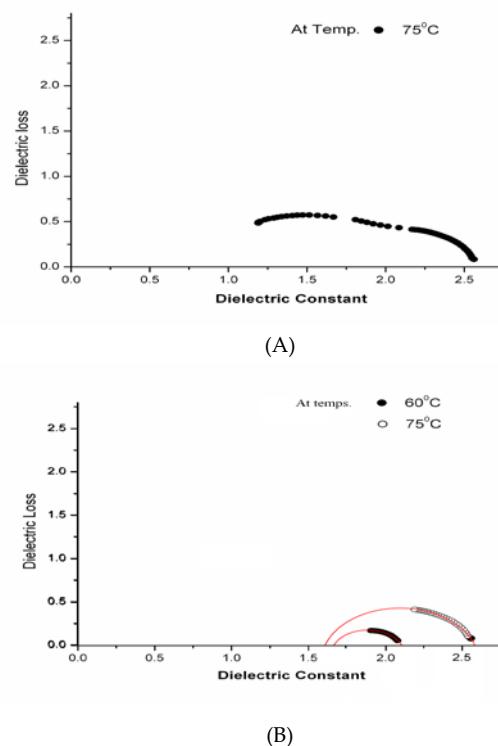


FIG. 2 (A) COLE COLE PLOT SHOWING DUAL SMECTIC PHASES (B) FITTED COLE COLE PLOT FOR BOTH

The Cole-Cole plot of the sample, while in the dual smectic phases, has been drawn at specific temperature 75°C as shown in figure 2(A). Figure 2(B), has been obtained from the best theoretical fitting of the Cole-Cole equation with the data, black circles represent experimental data while solid red line shows the best theoretical fitting data. Using such plots, values of dielectric parameters, such as the relaxation frequency, dielectric permittivity, activation energy and many more have been evaluated.

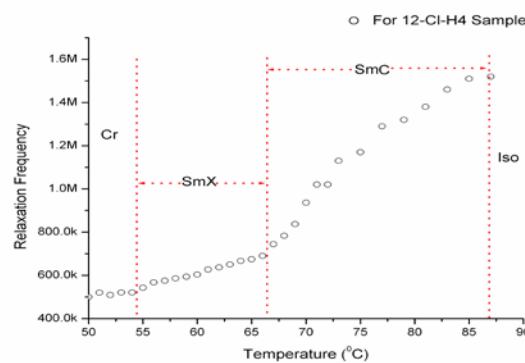


FIG. 3 VARIATION IN RELAXATION FREQUENCY WITH TEMPERATURE

Figure 3 shows the variation in relaxation frequency with temperature. Such relaxation studies provide

information about the molecular reorientation of the molecules. The observations suggest that the relaxation peak gradually increases with increment in temperature. The reason for this is the distortion in the shape of the molecules and thus relaxation processes exhibited may be correlated to the rotation of the side chain of the molecule. To explain it, a topological molecular arrangement is presented in figure 4.

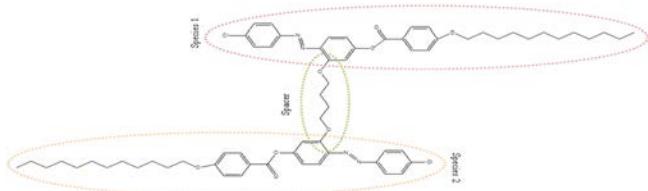


FIG. 4 SHOWS THE TWO DIFFERENT POSSIBLE CONFORMERS IN H SHAPED LIQUID CRYSTAL

In this mode, there are two possible conformers called Species1 (rod1) and Species2 (rod2) having two most preferred alignment directions of molecule. With increase in temperature, the rotation of molecules produces polarization which is in opposite direction vanishes and becomes minimum. Due to this reason relaxation peak has shifted toward higher side by presence of conformer's rotation in such a manner.

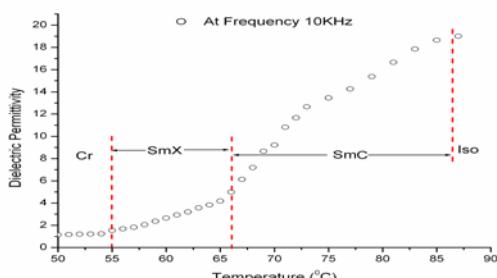


FIG. 5 VARIATION IN DIELECTRIC PERMITTIVITY WITH TEMPERATURE

The observed dielectric permittivity with variation in temperature has been shown in figure 5 suggesting that the dielectric permittivity increases up to a definite temperature compared to decrement at the clearing point or isotropic temperature, because in isotropic state molecule does not experience any force. Value of effective dielectric permittivity increases for the sample, showing slight change near crystal to SmX phase transition at 55 °C . Further increase in temperature, occurring and after 66 °C sample enters into SmC phase, and the reason behind this trend could be (the rotation of the side chains of molecules), the coupling between the orientational and

conformational order, due to the influence of flexible spacer. This also effects interlayer permeation of chain of molecules (the shorter tails and the longer tails co-exists along with a flexible spacer) causing correlation between cores in adjacent layers in SmC and SmX phase, which is influenced by the dimeric property of unusual shape of the liquid crystal molecule.

Relaxation strength as a function of temperature for the sample has been plotted in figure 6. The observed relaxation strength for the sample increases with increment in temperature. The relaxation strength of the sample slightly decreases at higher temperature due to zig-zag shape of molecule, which may result in the rotational freezing of the molecule , causing slight tilting of the molecule at higher temperatures.

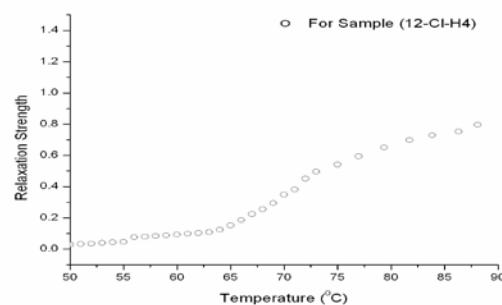


FIG. 6 RELAXATION STRENGTH WITH VARIATION IN TEMPERATURE

In our case, oxygen atom links the terminal chains to the core units in series, and addition of oxygen atom tends to bend the terminal chains away from the long axis of the central part of the molecule. Thus the molecule exhibits the zig-zag picture; and this unusual detailed investigation on single mesogen molecule reveals that zig-zag molecules can pack tightly into layers, but only if parts of the molecules are tilted relative to a line perpendicular to the layers.

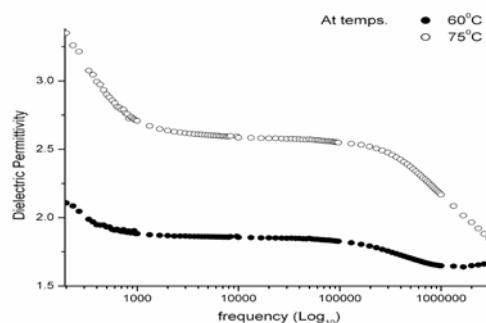


FIG. 7 BEHAVIOR OF DIELECTRIC PERMITTIVITY WITH VARIATION IN FREQUENCY

Figure 7 shows the variation in dielectric permittivity with frequency, initially, at lower frequency the trend

is same as observed in many liquid crystal samples and this is maintained due to "tumbling" motion- which can be co-related with the molecular rotation around the short molecular axis (LF process). Such motions are referred to as molecular "tumbling" where as when frequency is increased in SmC phase the same constant trend is observed but this time molecular rotation is around the long molecular axis (HF process). Such motions are referred to as spinning. This constancy in trend has been obtained due to the spacer attached between the two rod like molecules (species 1 and 2), which plays a vital role in maintaining constancy at higher and lower frequencies (flexible spacer group and length in A^0 , represented in structure).

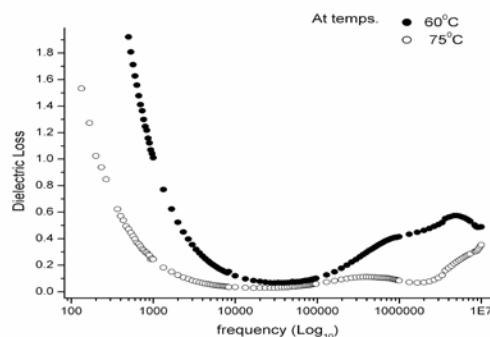
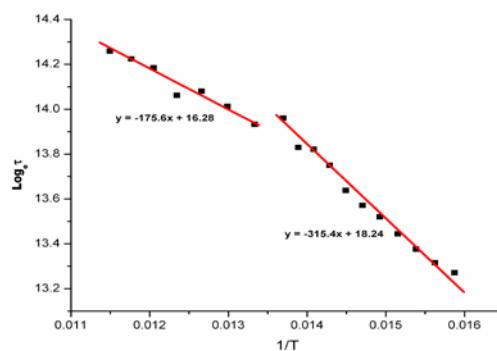


FIG. 8 BEHAVIOR OF DIELECTRIC LOSS WITH VARIATION IN FREQUENCY

Figure 8 represents the dielectric loss with variation in frequency. The dielectric loss curve has been plotted for both phases SmX and SmC. Dielectric loss of the sample having been examined in the sample is due to the mutual interaction between the permanent and the induced dipoles of the molecular sites, (lateral component in the molecule is essential to exhibit SmC phase), thus during the phase transition dipole moment (permanent and induced) plays a vital role and results in loss, exhibiting such a trend.

The Arrhenius equation describes the behavior for a process from one state to another separated by a potential barrier (Such as for example a double wall potential) and the height of the barrier is translated into the activation energy. In liquid crystal devices, the relaxation time is of extreme importance which further depends on the cell gap, the degree of molecular alignment and many other parameters. When a high voltage is applied to the sample cell, it affects relaxation time and all these properties depend on the activation energy, which plays a crucial role in many applications.



Therefore, activation energy has been calculated by using Arrhenius plot of the relaxation time Figure 9.

$$\tau = \tau_0 \exp(W_b/kT) \quad (4)$$

Where W_b is the activation energy, k is Boltzmann's constant and τ is the relaxation time. The activation energy for this sample is 15.15 meV in SmC phase and 27.20 meV in SmX phase.

As the fact that liquid crystal sample suffers from several defects, one of which is splay.

The Maier Saupe theory assumes that the force between liquid crystal molecules is a dispersion force which arises between two molecules that possess no permanent electric dipoles but induced electric dipoles. In fact , it has been observed that the average force experienced by a single molecule, due to other molecule can be derived using more forces than just the dispersion force because in our case molecules are not perfect rods and complete structures of the molecule are taken into account. Thus, splay defect suffering from many liquid crystalline systems can be minimized by utilizing the specific molecule, which is subject of this study.

Thus, on the basis of the proposed topological molecular model, it is predicted that the average force on each molecule is inversely proportional to the magnitude of the splay defect. For a sample, the rotation of side chain, the interlayer permeation of tails producing a correlation between cores in adjacent layers and with spacer, the unusual structure and most importantly, the relatively high average force experienced by each molecule in a bulk sample, all result in the reduction of the splay defect. Thus, it can be said that the average force on each molecule is inversely proportional to the magnitude of splay defect (in our case this average force is large as compared to other liquid crystal molecules). To overcome splay defect, molecules are arranged in a usual manner due to the average force experienced by the molecule helpful in reducing splay defect. Therefore,

this material could trigger a revolution in liquid crystalline devices.

Conclusions

Relationships between the molecular architecture and mesomorphic behavior are indubitable a subject of fundamental importance in the field of liquid crystals. In recent years, thermotropic mesogens with an unconventional molecular structure have drawn particular attention. In the present study, the dielectric study of unusual H-shaped liquid crystal exhibiting two mesophases (SmX and SmC) at different temperatures has been reported. The dielectric study of the samples has been done with the temperature and frequency variations. Relaxation frequency, relaxation strength increases with increment in temperature have been discussed. Activation energy has also been evaluated from Arrhenius plot, and various dielectric parameters have been studied. Further, a model has been proposed that explains the dielectric behavior of a bulk sample of these H-shaped molecules. In addition, from application point of view and how to overcome defects (splay), theoretical background has been described which could be vital in unusual Liquid crystals study.

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REFERENCES

- Andersch, J. and Tschiesske, C. "Synthesis and liquid crystalline properties of novel laterally connected twins." *Liquid Crystals* 21 (1996): 51- 63.
- Bailey, C., Fodor-Csorba, K., Gleeson, J.T., Sprunt, S.N. and Jakali, A. "Rheological properties of bent-core liquid crystals." *Soft Matter* 5 (2009): 3618-3622.
- Blinov, L.M. and Chigrinov, V.G. "Electro optic Effects in Liquid Crystal Materials." In New York: Springer- Verlag, 1994.
- Bottcher, C.J.F. and Bordewijk, P. "Theory of Electric Polarization." In Amsterdam: Elsevier, 1978.
- Brown, Glenn H., eds. "Advances in Liquid Crystal." In New York: Academic press, Vol. 2, 325-329, 1975.
- Chong, T.T., Heidelberg, T., Hashim, R. and Gary, S. "Computer modelling and simulation of thermotropic and lyotropic alkyl glycoside bilayers." *Liquid Crystals* 34 (2007): 267-281.
- Cole, K.S. and Cole, R.H. "Dispersion and absorption in dielectrics." *J. Chem. Phys.* 9 (1941): 341-351.
- Dhar, R., Gupta, M., Agrawal, V.K., Singh, M.K. and Singh, B. "Dielectric relaxation studies in N-(4-octyloxybenzylidene)-4-carbethoxyaniline." *Phase Transitions* 77 (2004): 375-384.
- Dhar, R., Srivastava, A.K. and Agrawal, V.K. "Induced twist grain boundary phase in the binary mixtures of cholesteryl caprylate and nonyloxybenzoic acid." *Indian J. Pure Appl. Phys.* 40 (2002): 694-700.
- Goodby, J.W., Mehls, G.H., Saez, I.M., Tuffin, R.P., Mackenzie, G., Velty, R.A., Benvegnu, T. and Plusquellec, D. "Liquid crystals with restricted molecular topologies: supermolecules and supramolecular assemblies." *Chem. Comm.* 70 (1998): 2057-2070.
- Govind, A.S. and Madhusudana, N.V. "A simple molecular theory of smectic-C liquid crystals." *Europhysics Letters* 55 (2001): 505-511.
- Kumar., Prajapati A.K., Varia, M.C. and Suresh, K.A. "Novel Mesogenic Azobenzene Dimer at Air-Water and Air-Solid Interfaces ." *Langmuir* 25 (2009): 839-844
- Manohar, R., Gupta, S., Prajapati, A.K., Patel, H.N. "Dielectric Relaxation Study of Two Different Mesogenic Cinnamates with a Substituted Ethyl Terminal Chain." *Molecular Crystals and Liquid Crystals* 548 (2011): 86-95
- Manohar, R., Misra, A.K., Singh, D.P., Yadav, S.P., Tripathi, P., Prajapati, A.K. and Varia, M.C. "Dielectric, thermal and optical study of an unusually shaped liquid crystal." *J. Phys. Chem. Solids* 71 (2010): 1684 -1689.
- Manohar, R., Srivastava, A.K., Jyotishman, Shukla J.P., Prajapati A.K. and Bonde N.L. "Dielectric, optical and thermodynamical properties of liquid crystal sample exhibiting SmA phase." *Int. J. Phys. Sci.* 1 (2006): 147-153.
- Meier, G., Sackmann, E. and Grabmaier, J.G. "Application of Liquid Crystals." In New York: Springer- Verlag, 1975.
- Newkome, G.R., Weis, C.D., Moorefield, C.N. and Weis, I. "Detection and Functionalization of Dendrimers Possessing Free Carboxylic Acid Moieties." *Macromolecules* 30 (1997): 2300-2304.
- Prajapati, A.K. and Patel, H.N. "Mesogenic cinnamates with a substituted ethyl terminal chain." *Liquid Crystals* 34

- (2007): 903-910.
- Rein and Demus D. "High pressure differential thermal analysis of laterally substituted nematic liquid crystalline compounds." *Liquid Crystals* 15 (1993): 193-202
- Varia, M.C., Kumar, S. and Prajapati, A.K. "H-shaped azoester-oxymethylene containing twin liquid crystalline compounds." *Liquid Crystals* 39 (2012): 365-371.
- Vill, V., Volkmar, Vill, Bocker T., Thiem, J. and Fischer, F. "The stereochemistry of glycolipids. A key for understanding membrane functions." *Liquid Crystals* 33 (2006): 1351-1358.
- Walba, D.M., Korblova, E., MacLennan, J.E., Link, D.R., Glaser, M.A. and Clark, N.A. "A Ferroelectric Liquid Crystal Conglomerate Composed of Racemic Molecules." *Science* 288 (2000): 2181-4.
- Yadav., Pandey K.K., Misra, A.K., Dixit, S. and Manohar, R. "Molecular dynamics in weakly polar nematic liquid crystal doped with dye." *Can. J. Phys.* 89 (2011): 661-665.
- Yoshizawa , Nakata, M. and Yamaguchi, A. "Phase transition behaviour of novel Y-shaped liquid crystal oligomers." *Liquid Crystals* 33 (2006): 605-609.

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His research interest involves the study of unusual shaped Liquid Crystal material. He is also interested to know the gamma radiation induced transformations in the properties of liquid crystal materials. He has also published many research papers in repute journals describing the properties of liquid crystals and gamma radiation induced modifications in the liquid crystal materials.



Dr. Rajiv Manohar obtained his Ph.D. degree in 1999 from University of Lucknow, Lucknow (India). Currently, he is an associate professor in the department of Physics, Lucknow University. His field of interest in research is the study and characterization of the pure and doped liquid crystals. He has published more than 70 international research papers in repute journal. He has also been awarded "Young scientist" by Indian Science congress and Indian liquid crystal society. He is a life member of International liquid crystal society, Indian liquid crystal society and Indian science congress. He is also a member of editorial board of some repute international journals.